

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-198141

(43)Date of publication of application : 11.07.2003

(51)Int.Cl.

H05K 3/46
C08G 59/18
C08L 29/14
C08L 61/06
C08L 61/28
C08L 63/00

(21)Application number : 2001-389954

(71)Applicant : HITACHI CHEM CO LTD

(22)Date of filing : 21.12.2001

(72)Inventor : FUJITA HIROAKI

OHASHI KENICHI

KUMAKURA YOSHITOSHI

(54) INSULATING MATERIAL FOR MULTILAYER PRINTED WIRING BOARD, INSULATING MATERIAL CLAD WITH METAL FOIL, AND MULTILAYER PRINTED WIRING BOARD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a low-cost adhesive film clad with a copper foil which enables processing of holes into a good shape by carbon dioxide gas laser processing and has a superior connection reliability, while at the same time satisfying various conventional characteristics such as an adhesiveness and a heat-resistant property, by increasing the toughness of a resin due to the increase in an aromatic component, a cross-linkage density, and the interlocking strength among high molecules by adding a cresol novolak type epoxy resin having a melting viscosity of 6.5P (150°C) or above with respect to a mixture of a carboxylic acid denatured polyvinyl acetal resin, a melamine resin, and a thermosetting resin.

SOLUTION: An insulating material for a multilayer printed wiring board is formed of a carboxylic acid denatured polyvinyl acetal resin, a melamine resin as a cross-linkage agent for a polyvinyl acetal resin, a thermosetting resin, and a cresol novolak type epoxy resin, as essential components.

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CLAIMS

[Claim(s)]

[Claim 1]An insulation material for multilayer printed wiring boards using melamine resin, thermosetting resin, and cresol novolak type epoxy resin as an essential ingredient as a crosslinking agent of carboxylic acid denatured polyvinyl acetal resin and polyvinyl-acetal resin.

[Claim 2]An insulation material for multilayer printed wiring boards being more than melt viscosity 6.5P (150 **) of cresol novolak type epoxy resin.

[Claim 3]An insulation material with a metallic foil which laminates the insulation material for multilayer printed wiring boards according to any one of claims 1 to 2 on a metallic foil by a semi hardened state.

[Claim 4]A multilayer printed wiring board, wherein an inner layer circuit formed in an inner layer circuit board by an insulating resin layer supporting an outer layer circuit consisting of the insulation material for multilayer printed wiring boards according to any one of claims 1 to 3 and an outer layer circuit are electrically connected.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the insulation material for multilayer printed wiring boards, the insulation material with a metallic foil which used this, and the multilayer printed wiring board using these.

[0002]

[Description of the Prior Art]In recent years, small weight saving [of electronic equipment], highly-efficient-izing, and low cost-ization advances, and the densification of wiring, slimming down of a substrate, high-reliability-izing of connection, and low cost-ization of manufacture are demanded also of the printed wired board used. When a multilayer printed wiring board is manufactured using the adhesive film which is prepreg without glass fabrics, or an adhesive film with copper foil, densification and small and light-ization are attained. Since it does not have glass fabrics, it excels also in byway drilling nature and laser hole processability. setting to manufacture of a multilayer printed wiring board especially -- the connection for the electrical link between layers -- it is an indispensable condition in order that it may realize high-reliability that drilling nature and laser hole processability are good since a detailed through hole and an interstitial viahole (IVH) are needed. Although the epoxy bonding film and the polyimide film were used conventionally, since it becomes a high cost, it is cheap and the adhesive film excellent in byway drilling nature and laser hole processability and the adhesive film with copper foil are demanded. The method of using the mixture of melamine resin and thermosetting resin as carboxylic acid denatured polyvinyl acetal resin and its crosslinking agent is known as a film shaped insulating material of low cost until now. However, since the section of the hole shape at the time of carbon-dioxide-laser processing served as overhang form (phenomenon in which resin for the mask edge direct lower part is scooped out in the case of laser processing by the conformal mask method), the fault of the sex with plating arose and there was a problem of being inferior to connection reliability.

[0003]

[Problem(s) to be Solved by the Invention]This invention was made in view of this situation, and receives the mixture of carboxylic acid denatured polyvinyl acetal resin, melamine resin, and thermosetting resin, When melt viscosity adds cresol novolak type epoxy resin more than 6.5P (150 **), An increase and crosslinking density of an aromatic component, and polymers chains twining, attaining toughening of resin by the increase in sexual, and satisfying various characteristics, such as an adhesive property from the

former, and heat resistance, the hole shape at the time of carbon-dioxide-laser processing is good, and aims at providing the cheap adhesive film with copper foil excellent in connection reliability.

[0004]

[Means for Solving the Problem] That is, this invention is attained when melamine resin, thermosetting resin, and melt viscosity use cresol novolak epoxy resin more than 6.5P (150 **) as an essential ingredient as a crosslinking agent of carboxylic acid denatured polyvinyl acetal resin and polyvinyl-acetal resin.

Hereafter, this invention is explained in detail.

[0005](Polyvinyl-acetal resin) In this invention, especially a thing for which carboxylic acid denatured polyvinyl acetal resin is used is preferred as polyvinyl-acetal resin. Although a degree of polymerization of carboxylic acid denatured polyvinyl acetal resin and the degree of acetalization in particular are not limited in this invention, average degrees of polymerization are 500-3000, and that whose degree of acetalization is 60-100-mol% is preferred. If less than 500 are not enough as the heat resistance of adhesives as for an average degree of polymerization and it exceeds 3000, it will become difficult for viscosity of adhesives to become high too much and to apply to a metallic foil. Especially if the degree of acetalization is the above-mentioned range, it is not restricted, but less than, less than [60mol%] is inferior to adhesive strength in it rather than it is enough as the pliability of resin. As for carboxylic acid denatured polyvinyl acetal resin, it is preferred especially from a point of uniform thickness and heat resistance to use it five to 50% of the weight to the whole pitch (a hardening agent and a hardening accelerator are included) of an insulation material for multilayer printed wiring boards in this invention. If there is too little carboxylic acid denatured polyvinyl acetal resin, an insulating layer of uniform thickness will become is hard to be obtained, and when too large, there is a tendency for heat resistance etc. to fall. Polyvinyl-acetal resin, such as a polyvinyl butyral which has not denaturalized with unsaturated carboxylic acid which has two or more carboxyl groups, can also be mixed and used together. As carboxylic acid denatured polyvinyl acetal resin, S lek KS-23, HS-1 (all are the Sekisui Chemical Co., Ltd. make and a trade name), etc. are mentioned by what is marketed. S lek KS-3Z, KS-5, and KS-5Z (all are the Sekisui Chemical Co., Ltd. make and a trade name) etc. are mentioned. Polyvinyl butyral resin which has not denaturalized with unsaturated carboxylic acid which has two or more carboxyl groups can also be mixed and used together. Independent, two or more kinds are mixed, and these resin is used.

[0006](***** material of polyvinyl-acetal resin) A crosslinking agent of polyvinyl-acetal resin can be blended with an insulation material. When acid denaturation especially of the polyvinyl-acetal resin is not carried out, a crosslinking agent serves as an essential ingredient. As ***** material of polyvinyl-acetal resin, Resol type phenol resin, phenol resin, melamine resin, the Polly (or di-) isocyanate compound, It is preferred to use methylol-ized melamine resin by which could use GURIOKI Southall or these derivatives and alkoxy ** was carried out in methylol-ized melamine resin and alcohol. As for ***** material, it is preferred to use in the range of one to 100 weight section to polyvinyl-acetal resin 100 weight section. In less than one weight section, if there is a tendency for polyvinyl-acetal resin to carry out bridging injury shortage, and for chemical resistance etc. to fall and 100 weight sections are exceeded, the inner layer circuit restoration nature of an insulation material at the time of multilayering and heat resistance may fall.

[0007](Cresol novolak type epoxy resin) It may have two or more epoxy groups in intramolecular, and as long as melt viscosity is cresol novolak type epoxy resin more than 6.5P (150 **), what kind of thing may be used. These halogenides, a hydrogenation thing, and a mixture of said resin are suitable. As for cresol

novolak type epoxy resin, it is preferred to use in the range of 50 to 150 weight section to polyvinyl-acetal resin 100 weight section. In less than 50 weight sections, if good beer shape is not obtained and 150 weight sections are exceeded, the inner layer circuit restoration nature of an insulation material at the time of multilayering and heat resistance may fall.

[0008](Thermosetting resin) As long as it is a compound which has two or more epoxy groups in intramolecular as thermosetting resin, what kind of thing may be used, For example, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, A bisphenol smooth S form epoxy resin, glycidyl ester typed epoxy resin, Glycidyl amine type epoxy resin, a hydantoin type epoxy resin, an isocyanate type epoxy resin, an aliphatic series annular epoxy resin, a hydrogenation thing, and a mixture of said resin are preferred, and a bisphenol A type epoxy resin is excellent in flammability-proof or heat resistance, and especially preferred.

[0009](Hardening agent) If it usually uses for hardening of an epoxy resin, there will be no restriction in particular in a hardening agent, For example, a halogenide of dicyandiamide, bisphenol A, polyvinyl phenol, phenol novolak resin, bisphenol A novolak resin, and these phenol resin, a hydride, etc. can be used.

[0010](Hardening accelerator) As a hardening accelerator, when resin is an epoxy resin, an imidazole compound, an organophosphorus compound, tertiary amine, quarternary ammonium salt, etc. can be used. The range of 0.01 to 20 weight section is preferred to resin 100 weight section, and a rate over the above-mentioned resin of this hardening accelerator has the more preferred range of 0.1 to 1.0 weight section.

[0011](Diluent) A resinous principle (***** material, a hardening agent, and a hardening accelerator are included) of this invention can be diluted with a solvent, and can also be used as resin varnish. Acetone, methyl ethyl ketone, toluene, xylene, methyl isobutyl ketone, ethyl acetate, ethylene glycol monomethyl ether, methanol, ethanol, N,N'-dimethylformamide, N,N'-dimethylacetamide, etc. can be used for a solvent.

[0012](Other combination drugs) In this invention, a coupling agent, a filler, etc. other than each ingredient above-mentioned in resin may be blended further suitably if needed.

[0013]Thus, by applying and drying to metallic foils, such as copper foil, with a gestalt of a varnish, an insulation material obtained can be made into a semi hardened state, and can be used as an insulation material with a metallic foil. Since adhesive strength with an insulation material is increased, that [a metallic foil's] to which roughening treatment of the surface is carried out is preferred. A multilevel-metal tension laminate sheet containing an inner layer circuit board is producible by laminating and carrying out heat pressing of the insulation material with a metallic foil again so that an insulation material may face an inner layer circuit board by applying an insulation material to an inner layer circuit board, and laminating and carrying out heat pressing of the metallic foil to it. An inner layer circuit formed in an inner layer circuit board in accordance with a conventional method by giving a formation process of an outer layer circuit and a flow process of an inner layer circuit and an outer layer circuit in this and an outer layer circuit can produce an electrically connected multilayer printed wiring board.

[0014]

[Example]Hereafter, although the example of this invention and its comparative example explain concretely, this invention is not limited to these examples. The resin composition was used at a rate shown in Table 1 using the following raw material.

- Bisphenol A type epoxy resin (1250 weight per epoxy equivalent molecular weight 208)
- Cresol novolak epoxy resin (ESCN-190-[the P weight per epoxy equivalent 198 and] 10: ESCN-190-[the P weight per epoxy equivalent 195 and] 6: ESCN-190-3: melt viscosity 2.8 melt viscosity 6.5 melt viscosity 10P and weight per epoxy equivalent 199: Sumitomo Chemical make)
- Carboxylic acid denatured polyvinyl acetal resin (S lek KS-23Z: made by Sekisui Chemical)
- Epoxy curing agent (Dicy: Nippon Carbide Industries)
- Imidazole series hardening accelerator (P-200Z50P: Japan epoxy resin)

[0015]Example 1 bisphenol-A-type epoxy resin 300 weight section, cresol-novolak-epoxy-resin (ESCN-190-10) 100 weight section, Methyl ethyl ketone and methanol were added to the constituent of dicyandiamide 10 weight section, 2-ethyl-4-methylimidazole 0.6 weight section, and carboxylic acid denaturation polyvinyl-acetal 100 weight section, and 65% of the weight of the varnish was adjusted. This varnish was applied so that the insulation material thickness after drying to the roughened surface of 12-micrometer-thick one side roughening copper foil might be set to 60 micrometers, and it was dried, and the insulation material with copper foil of the semi hardened state was obtained. To both sides of the inner layer circuit board which performed circuit processing to the double-sided copper-clad laminate sheet with a copper foil thickness of 35 micrometers at 0.2 mm in thickness. The insulation material with copper foil produced previously was laminated so that an insulation material might face an inner layer circuit board, for 185 ** and 60 minutes, on condition of product pressure 3.0MPa, it molded by heating under pressure and the multilayer [containing an inner layer circuit] copper-clad laminate sheet was produced. After forming the window hole for laser processing in outer layer copper foil of a copper-clad laminate sheet by a publicly known method, IVH was formed by carbon-dioxide-laser exposure (8 microseconds of BARUSU width, two shots), and the copper-clad laminate sheet was manufactured. The following evaluations were performed to the copper-clad laminate sheet which produced [above-mentioned].

- 1) Tg of the resin curing thing by a dynamic viscoelasticity measuring device (DVE) was measured.
- 2) The formed beer shape (existence of an overhang) was observed by section polish.
- 3) The 100-micrometer-wide copper circuit and the diameter of a viahole of 150 micrometers by after outer layer copper foil etching, After forming a viahole with a land diameter of 350 micrometers, the spalling test of 125 ** (30 minutes) x 300 cycles was carried out from -65 ** (30 minutes), and section observation estimated the crack generation existence during insulation material-plating.

[0016]In accordance with the same method as Example 1, it evaluated except having changed the molecular weight of example 2 cresol-novolak-type-epoxy-resin (ESCN-190-6) 100 weight section.

[0017]In accordance with the same method as Example 1, it evaluated except having removed comparative example 1 cresol novolak type epoxy resin (ESCN-190-10).

[0018]In accordance with the same method as Example 1, it evaluated except having changed comparative example 2 cresol-novolak-type-epoxy-resin (ESCN-190-3) 100 weight section.

[0019]

[Table 1]

	実施例 1	実施例 2	比較例 1	比較例 2
クレゾールノボラック型エポキシ樹脂 (BSCN-190-3)	—	—	—	100
クレゾールノボラックエポキシ樹脂 (BSCN-190-5)	—	100	—	—
クレゾールノボラックエポキシ樹脂 (BSCN-190-10)	100	—	—	—
ポリビニルピチラール樹脂	100	100	100	100
ビスフェノールA型エポキシ樹脂	300	300	400	300
T _g (°C) (DVE)	143	139	123	130
ビア形状	○	○	×	×
熱衝撃試験	○	○	×	×

Beer shape: O (with no overhang form), ** (overhang form is shown a little), x (overhang form)

Spalling test: O (with no interface crack), x (those with an interface crack)

[0020] Examples 1-2 have high T_g so that clearly from the above result. Since the copper-clad laminate sheet manufactured using this has good beer shape, it excels in connection reliability.

It is cheap and useful as a reliable insulation material for multilayer printed wiring boards.

[0021]

[Effect of the Invention] With the insulation material for multilayer printed wiring boards in this invention, beer shape is good, and it excels in connection reliability, and the multilayer printed wiring board using the insulation material with a metallic foil and this insulation material with a metallic foil of low cost can be provided.

[Translation done.]